Solution behaviour of mixed surfactant systems in the presence of electrolytes and their effect on oscillatory rheological properties of sodium carboxymethyl cellulose

Thesis Submitted by

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In fulfilment for the award of the Degree of

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Under the Guidance of

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CERTIFICATE

This is to certify that the project report entitled, "**Solution behaviour of mixed surfactant systems in the presence of electrolytes and their effect on oscillatory rheological properties of sodium carboxymethyl cellulose**" submitted by Vijay Bhate in fulfilment for the requirements for the award of Master of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

Data on critical micelle concentration (CMC) of mixed surfactant system containing solution of CTAB + IGEPAL CO 890 have been evaluated as a function of mole fraction of CTAB. The results have been studied in terms of Rubingh's theory and the interaction parameter (β) has been calculated. Experimental values of mixed surfactants 3:7 and 7:3 has been evaluated as 0.1 and 0.2 mM respectively, which is lower than the theoretical values. Thus, best suited for solution parameter analysis and further rheological properties is 3:7. Simultaneously the effect of mixed surfactant solutions on rheological properties of carboxymethyl cellulose also has been studied by using different sweep analysis; frequency, amplitude. The study of moduli; storage (G') and loss (G") modulus exemplifies the elastic behaviour of mixed surfactant over natural additive cmc. Further, the study has been extended to the effect of electrolytes addition with mixed surfactants for higher end application at food, cosmetics industries.

***Keywords**:* Cationic surfactant, Surface tension, Wilhelmy plate tensiometer, Electrolyte, Langmuir adsorption isotherm, Storage modulus.

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NOMENCLATURE

CMC	Critical Micellar Concentration
cmc	carboxymethyl cellulose
CTAB	Cetyl trimethylammonium bromide
NaCl	Sodium Chloride
Na_3PO_4	Sodium Phosphate
Na_2SO_4	Sodium Sulphate
IFT	Interfacial tension
T	Temperature
P	Pressure
UV	Ultraviolet
DST	Dynamic Surface tension
SDS	Sodium dodecyl sulphate

LIST OF SYMBOLS

Γ	Surface excess concentration
C	Concentration of surfactant in liquid phase at adsorption equilibrium
C*	CMC of mixed surfactant
œ	Mole fraction of surfactant
ω	Area covered by one molecule in a surface layer
G	Gibbs free energy
R	Universal gas constant
∏	Surface pressure
τ	shear stress
K	consistency index
y	shear rate
A	An interfacial area
ɵ	Surface coverage
(G')	Storage Modulus
(G")	Loss modulus

CHAPTER 1

INTRODUCTION

INTRODUCTION

1.1 Solution behaviour of surfactant

Surfactants are organic compounds that are polar in nature and contain a hydrophilic part and a hydrophobic part. They are amphiphilic in nature, so they are more suitable for different applications [1]. As both hydrophilic and hydrophobic heads are present, therefore, a surfactant contains both water-insoluble component and water-soluble component. However, they have a potential to change surface tension. When surfactants are added to liquid, its surface tension goes on decreasing with the concentration of surfactant till CMC where micelles formation occurs [2].

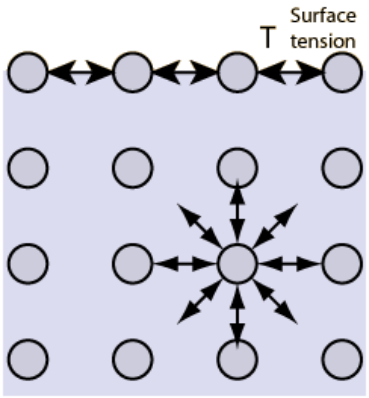

Figure 1.1 Schematics of Surface Tension

CMC is critical micelle concentration above which micelles form and all addition of surfactant work to the micelles. During this phenomenon, number of surfactant molecules will get adsorb at the interface, so the overall free energy of the system is lowered. Basically, non-ionic and ionic surfactants change the surface tension but the ionic surfactant has properties of counter ion binding and surface electric potential, so they are more effective in lowering the surface tension. Surfactants having hydrophilic head; cationic surfactants have very low CMC [3] and can be used even in hard water. Surface tension is significant in large number of applications in food processing, pharmaceutical, medicine science, packaging products, etc.

1.2 Mixed surfactant system

Currently, in many practical applications molecular-molecular interaction plays important role. So, mixtures of surfactant have been studied to understand molecular interaction between different surfactants in practical applications. Interaction between ionic and non-ionic surfactants in an adsorbed film and micelle is larger than that between anionic and

anionic surfactants or cationic and cationic surfactants and that between nonionic surfactants. Generally industrial surfactant or mixed surfactant systems are the mixtures of electrolytes, dyes, fillers. Especially these species are added to achieve certain synergetic effect in pH, viscosity and other physicochemical properties of the system [4-5]. Hence, we can achieve surface properties for particular application by changing the composition of this system. Generally, to find appropriate surfactant system requires the basic understanding of the adsorption phenomenon and interaction between in these systems. In other words, a theoretical model of the adsorption process in mixed systems is required. It is generally concluded that the polar head group non-ionic surfactant attracts inorganic cations in adsorbed films and micelles, thus difference in the size of head group between ionic and non-ionic surfactants is favourable for the packing of the surfactants, and a counter ion with a large hydration radius is less effective than that with a small hydration radius for the shielding of the charge on the ionic head group of surfactant in adsorbed films and micelles and causes large interaction between the head groups of ionic and non-ionic surfactants**.**

1.3 Importance of mixed surfactants system

In most of the practical applications, we find the mixture of surfactants is favoured rather than individual surfactant. As the suitability of mixed surfactant as detergents, wetting agents, emulsifiers, foaming agent get increased. The properties and behaviour of a mixture are quite different from that of individual surfactant and in some case synergistic effects are observed. We can decrease the environmental impact of surfactant by using known mixtures of surfactants whose interfacial properties exhibit synergism. Consequently, the amount of surfactant required is less for mixture with synergism. The superior properties of mixed surfactants like low production cost make them more economically stable.

1.4 Rheology

Rheology is the study of the flow of matter, primarily in a liquid state. It also studies the 'soft solids' or solids under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force. It applies to substances which have a complex microstructure such as muds, sludge, suspension, emulsion as well as many foods and additives, and other biological materials or other materials which belong to the class of soft matter. Newtonian fluids can be characterized by a single coefficient of viscosity for a particular temperature. Although this viscosity will change with temperature, it does not change with the strain rate [6]. Only some fluids exhibit such constant viscosity. The large class of fluids whose viscosity changes with the strain rate (the relative velocity of flow) are

called non-Newtonian fluids. The experimental characterization of a material's rheological behaviour is known as rheometry. Important aspects of the rheology are Flow behaviour of material and its internal structure (e.g. the orientation and elongation of polymer molecules). Rheology accounts for the action of non-Newtonian fluids, by characterizing the minimum number of functions that are needed to relate stresses with the rate of change of strains or strain rates [7]. Extensional rheology refers to study of extensional flows. Basically, much more experimental data available on shear flow, thus it's easy to study.

1.5 Importance of Rheology

Understanding the mechanism of surfactant adsorption at the fluid interface is a central proposal in the knowledge of their functionality and applications [8-9]. Nowadays, there are many fundamental and applied dynamics process for which the characterization of adsorbed interfacial layers of surfactant and polymer molecules is very essential. These contain foaming and emulsification that are widely used in the production of cosmetics, pharmaceuticals and food, mining, oil industry, etc. Currently there is a significant interest in industrial applications, studying dynamics of interfacial layers. These studies are much useful in understanding the interaction between molecules, change of molecular conformation or molecular aggregations. Currently rheology also plays a much important role in food product design. The microstructure of liquid [10] foods has played an important role in its quality and quantity. Microstructures play an important role in understanding the physic-chemical bonds and inter/intra molecular associations between the ingredients in any recipe. Flow characteristics of the material influenced by microstructures. For example viscosity and elasticity that is much important in heat and mass transfer.

Principally rheology worried with snowballing nonstop mechanics to portray the flow of material. Generally it characterises the elastic, viscous and plastic behaviour of material. Rheology can easily predict the mechanical response based on nano- or microstructure of the material, e.g. the molecular size and architecture of polymers in solution. Materials with the appearances of a fluid will drift when exposed to the tension that is force per unit area. There are altered types of stress (like shear, torsional, etc.), and materials can return inversely to changed pressures. Imaginary rheology is much disturbed with peripheral forces and torques with core strain rises and flow rates.

Rheology syndicates the seemingly unrelated fields of malleability and non-Newtonian fluid subtleties by knowing that materials experiencing these types of deformation are unable

to provision a stress in static steadiness. So, a solid undergoing plastic deformation is a fluid. Rheology also helps to establish the relationships between deformation and stresses, by correct measurements.

1.6 Objective of the project

The prime objective of present investigation deals with the study of solution and rheological properties of mixed surfactant of CTAB-IGEPAL CO-890 with the determination of solution parameters and oscillatory rheological studies. The effect of mixed surfactant in the presence and absence of mono-, di-, tri- valent electrolytes has been studied over the natural polymer carboxymethyl cellulose for higher end applications and further fundamental studies on interfacial and emulsion rheology.

CHAPTER 2

LITERATURE SURVEY

2.1 Critical Micelle Concentration (CMC) of mixed surfactants.

The mixed surfactant systems always show the different character that provides large number of applications in current scenario. These applications include oil recovery, drug delivery, detergency, froth floatation, etc.

Table 2.1 Previous studies on CMC of mixed surfactants.

Mixed surfactants system	**Characterization Parameters**	**Applications**	**Reference**
CTAB (Cationic) and Nonyl phenyl ethoxylates (Nonionic)	Surface tension, relative viscosity, NMR	Cosmetics, Drug Delivery	Desai et al. [11]
Nonylphenol polythoxylate (Nonionic) and Sodium dodecyl sulfate (Anionic)	Surface tension	Food Grade Emulsions	Li-Jen Chen et al. [12]
Tetradecylpyridinium bromide (Cationic) and Triton-X-100 (Nonionic)	Surface tension	Phase behaviour	Parihar et al. [13]
N-N dimethyl-N-lauroyl lysine (Amphoteric) and Sodium dodecyl sulfate (Anionic) and inorganic electrolytes.	Surface tension, pH, relative viscosity	Food grade microemulsions	ABE et al. [14]
SDS (Anionic) and CTAB (Cationic)	Pyrene intensity ratio	Iron nanoparticles production	Alargova et al. [15]
N,N'-bis(dimethyldodecyl)-1,2 ethanediammoniumdibromide (12-2-12) and N,N'-bis(dimethyldodecyl)-1,4-butanedi-ammoniumdibromide (12-4-12)	Surface Tension, Phase behaviour test, surfactant-surfactant interaction in micelles	Enhanced oil recovery	Parekh et al. [16]
CTAB (Cationic) and Triton-X-100 (Nonionic) with Sodium Bromide.	Surface Tension, EMF measurements.	Cosmetics, Drug Delivery	Javadian et al. [17]
SDS (Anionic) and Polyoxyethylene (Nonionic)	Surface Tension, Conductivity.	Food Grade Emulsions	Yow-Lin et al.[18]

Above all studies shows the how CMC of individual surfactant affects when mixed with another surfactant. According to Desai et al. [11] the superior properties of mixed surfactants can be used to low down the production cost. The CMC ethics of a mixture are much lower than those prophesied by ideal solutions theory. Javadian et al. [17] considered the effect of electrolyte on CMC of mixed surfactants. As industrial surfactant systems archetypally contain altered ionic and non-ionic surfactants, electrolytes, dyes. Sometimes to control ionic strength, pH, viscosity some species are added. ABE et al. [14] described the adsorption spectacle in these systems. As ABE et al. found that termination temperature of diverse surfactant results is helpless on the kinds of inorganic electrolytes. He also restrained the effect of inorganic electrolytes and pH on a mixed micelle foundation of amphoteric and anionic surfactant system in terms of surface tension, pH and relative viscosity.

Parekh et al. [16] also studied the synergistic interaction of mixed surfactant system. Surface tension measurement studied the mixture of anionic-cationic surfactant at the different molar ratio. Various parameters like CMC, exterior excess meditations, lowest area per molecule, and interaction parameter of mixed micelle have been considered using different approaches. Alargova et al. [15] naturally investigated the critical micelle concentration and micelle aggregation sum of various conservative surfactant and dimeric anionic and cationic surfactants by electrical conductivity, spectrofluorometry. Instantaneously he carried out the effect of mixture composition on the mixed micelle aggregation number. Also, Alargova compares non-ionic conventional surfactant with ionic surfactant. Parihar et al. [13] also studied mixed micellization process of binary mixtures designed by surfactants. Also, he examined the mixed CMC values by surface tension method to gain the same effect for the combination with synergism than without synergism and phase behaviour.

2.2 Effect of mixed surfactant solutions on the rheology of different additives

In literature, there are many publications on the effect of surfactant on rheological properties of the oil-water emulsion. Also the effect of surfactant on equilibrium adsorption properties, i.e. adsorption isotherms (Lyklema J. et al. [14]). These investigations are dedicated to the interfacial viscoelastic behaviour, changes in the interfacial properties, oscillatory shear properties. In a current industrial scenario, it's quite essential to learn synergism of mixed surfactants. The number of researchers studied mixed surfactant systems with different additives to find out rheology and its effect on the emulsion. Currently rheology has number of applications like Thickening and dewatering of mineral slurries, paint manufacture,

cosmetics industry. So, in order to get better synergism with mixed surfactants, many researchers investigated the effects of polymer, electrolytes, emulsifying agent on it.

Table 2.2 State of art on effect of mixed surfactant systems on rheology of different additives

Mixed surfactants system	**Rheological Parameters**	**Applications**	**Reference**
SDS (anionic) and AOT (anionic) with polymers.	Viscosity, EMF measurement, Binding isotherms	Thickening and dewatering of mineral slurries.	Kwak et al. [19]
Sodium Naphthalene sulfonate (anionic) and sugar based co-surfactants with gelatin.	Surface tension, Shear viscosity, stress-strain.	Filtration, soil chemistry.	Howe et al. [20]
Dodecyl-dimethyl phosphine oxide and proteins	Surface tension, Oscillatory Rheology	Paint manufacture, food chemistry.	Lotfi et al. [21]
Polyxyethylene 20 sorbitan monooleate and sorbitan monooleate (non-ionic)	Droplet size measurement, temperature dependency, stability measurement	Cosmetics chemistry.	Noor El-Din et al. [22]
SDS and AOT (Anionic)	Dilational rheology, shear rheology	Polymer chemistry.	Miller et al. [23]
Decyl and tetradecyl dimethyl phosphine oxide (non-anionic)	Viscoelasticity modulus, phase angle	The reaction involving mineral slurries like gold extraction.	Kovalchuk et al. [24]
DTAB (Cationic) with DNA from calf and NaBr	Surface shear rheology, Complex modulus. Flow measurement	Forming materials like a brick.	Langevin et al. [25]
SDS (Anionic) and lysozyme (protein)	Surface Tension, Conductivity.	Food dispersion formulation, Texture	MaldonadoValderrama et al.[26]

Kwak et al. [19] studied the rheology and binding mechanisms in the aqueous system of hydrophobically modified acrylamide and acrylic acid copolymers and surfactants. Also, he studied the effect of the interaction between surfactants with terpolymers contain hydrophilic and hydrophobic heads. On comparing Kwak found that anionic surfactants have strong interaction with the terpolymer, thus they show substantial viscosity enhancements in solution. At the same time cationic surfactants results in precipitation of the terpolymer/surfactant compound before reaching the CMC. According to Howe, et al. [20] mono and di-alkyl sugar co-surfactants stand ample operative at dipping the shear viscosity and shear thinning performance of oil-water emulsion stabilized by anionic surfactant. Howe suggested how the efficiency of each co-surfactant depended on alkyl chain length. Also, he suggested mono-alkyl chain bounces recovering outcomes than the di-alkyl chain. Lotfi et al. [21] also premeditated the outcome of non-ionic surfactants on adsorption of proteins in solution. All measurements performed by buoyant bubble profile method where the bubble formation is rapid. Lotfi also showed the stimulus of proteins on dynamic surface tension; this is unpaid to enlarged surface activity of the proteins in the occurrence of trivial total of surfactants. He also studied the dilatation rheology of mixed protein/surfactant at very low concentration.

According to Noor El-Din et, al. [22] rheological behaviour of water in the diesel fuel emulsion is highly influenced by the amount of surfactant. He also investigated how nano-emulsions exhibit low viscosity Newtonian character. On other hands, he proved how viscosity decreased on ageing of emulsion due to Ostwald ripening. Miller et al. [23] studied the interfacial rheology of mixed layers of food proteins and surfactants. By comparing with different proteins, he suggested some ideal frequencies for dilational studies. Kovalchuk et al. [24] investigated the surface dilational rheology of mixed surfactant layers at the liquid interface. He also studied the dilational rheology of surfactant mixtures at low frequencies, as provided by drop and bubble profile analysis tensiometry. On other hands, he explained the adsorption characteristics of surfactants in solution. Langevin et al. [25] reveals the difference in shear behaviour between surfactant of opposite charge and surface layers containing polyelectrolytes. He also studied the surface action under shear deformation. Langevin also studied the same phenomenon as Regismond et al. [27]; surface shear properties can be qualitatively measured by the simple test, examining the motion of talc particle. Maldonado-Valderrama et al. [26] has planned the interfacial rheology of protein and surfactant blends. He also determined the distribution of protein and surfactant at the fluid interface by competitive adsorption between two types of emulsifiers.

CHAPTER 3

EXPERIMENTAL WORK

This section directed on tentative measures and trialling tracked in the project. The surface tension magnitudes of mixed surfactants persisted done consuming Wilhelmy plate tensiometer at ambient environments of pressure and temperature. All the values of surface tension measured over some time using the instrument. The rheological study of individual surfactant and mixed surfactants was also done by using TA HR-2 hybrid rheometer for mixed surfactants with over define time at various modes and temperature ranges.

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3.1 Materials

Cationic surfactant Cetyl trimethyl ammonium bromide (CTAB, purity >99%) and non-ionic surfactant IGEPAL CO-890 were purchased from Sigma-Aldrich. Carboxymethyl cellulose sodium salt was purchase from LOBA Chemicals. The salts used were sodium chloride and sodium sulphate was purchased from RANKEM Chemicals (99.5% pure). Sodium di-hydrogen phosphate was purchased from Merck Millipore. Anhydrous Ethanol stood since Merck. All reagents stayed castoff as established without further sanitisation. Ethanol was hand-me-down for cleaning purposes.

3.2 Properties of Surfactants Used

Cetyl trimethylammonium bromide (CTAB) is a cationic surfactant which needs a molecular weight of 364.5g/mol and molecular formula $(C_{16}H_{33})N(CH_3)_3Br$. It is well soluble in water and has a tall lenience for salts. It has a molecular building as shown in figure 3.1. The CMC value for CTAB is 0.98 mM or 0.357 g/l.

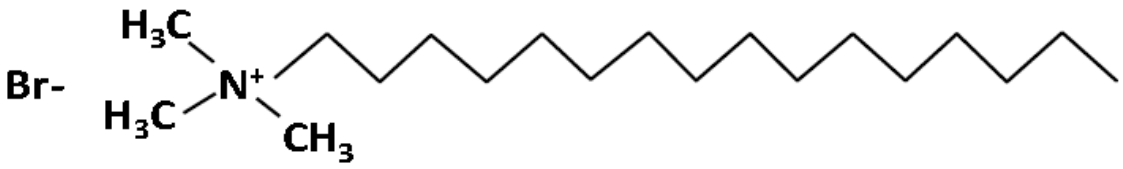


Figure 3.1 Molecular Structure of CTAB.

IGEPAL CO-890 is a non-ionic surfactant which needs a molecular weight of 1982 g/mol and molecular formula $(C_2H_4O)_n \cdot C_{15}H_{24}O$ where n=40. It is a handy emulsion polymerization surfactant which is container be cast-off as latex post stabilizer. It is also charity as sole-emulsifier and co-emulsifier. It has the molecular structure as shown in figure 3.2.

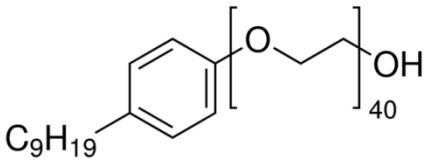


Figure 3.2 Molecular Structure of IGEPAL CO-890.

3.3 Surface Tension Measurements

3.3.1 Principle of Wilhelmy plate Tensiometer

Surface tension measurements at the air-liquid boundary remained done with a Pt Wilhelmy plate on a surface tensiometer (Dataphysics, Filderstadt, Germany, DCAT 11EC) which is shown in figure 3.3.

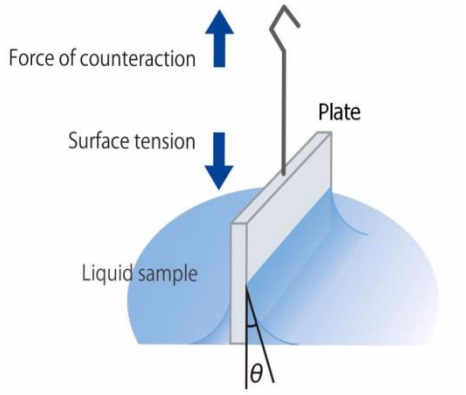


Figure 3.3 Principle of Wilhelmy plate tensiometer

The Wilhelmy plate technique is a meek method but entails careful hands to measure the Surface tension as the plate is actual gentle. It is a thin plate of order few square centimetres in the area. The plate is generally made up of filter paper, glass or platinum which may be roughened to ensure complete wetting. In this method, the plate is placed in such way that it is perpendicular to the interface and the force exerted on it is measured. In fact, all measurement results are irrelevant to the material until the material is wetted by the liquid. Then the force acting on plate due to wetting is measured via a tensiometer and used to calculate the surface tension by Wilhelmy equation,

$$\gamma = \frac{F}{4\pi r}$$

The platinum plate was plentifully bathed with water tracked by alcohol and flamed before and later respectively quantity.

3.3.2 Procedure of Surface Tension Measurement

Preparation of solutions

Different solutions with a molar concentration of 10 mmol having a ratio (CTAB to IGEPAL) of 0:10, 3:7, 7:3, 10:0 solutions were prepared by adding required amount of surfactants to a specific volume of water in a beaker. The beakers were sonicated in a sonicator till the solutes completely dissolve, and they were transferred to a volumetric flask and the total volume is made up to 50ml. Different solutions of each of the salts with the molar concentration of 1mmol were prepared by adding required amount of electrolytes to a specific a volume of water in a beaker. The beakers were sonicated in a sonicator till the solutes completely dissolve. Later they were transferred to a volumetric flask, and the total volume is made up to 50ml.

Preparation of cmc (Carboxymethyl Cellulose):

Carboxymethyl cellulose (cmc) with a viscosity range of 2-4 centipoise used in the present work was supplied by Loba Chemical Company. Aqueous solutions of 2 wt% cmc stayed organized by dissolving the appropriate amount of cmc in distilled water at room temperature. To study the effect of surfactants, different molar concentrations of above prepared surfactants ranging from values below CMC (0.01 mM), at CMC as well as above CMC (4 times cmc) were added with the required amount of cmc to maintain 2 wt%. To study the effect of electrolytes on cmc, different solutions were prepared by adding 150 mM of three different electrolytes along with the surfactants at 0.01mmol, maintaining 2wt% of cmc in the solution. Former tests exhibited that the grounding of cmc solutions requires a minimum time to dissolve fully the cmc powder. This time is contingent on the polymer concentration as well as stirring time. No external power or heat was supplied for mixing as it may depolymerise the solution.

Measurement of surface tension

The surface tension of completely aqueous phase at unalike attentiveness was indomitable as a purpose of mole fraction of CTAB. Firstly aqueous phase was first put into the vial, and then the plate was carefully cleaned and put into the probe. Utmost care needs to be taken while placing the plate into the probe. Then the surface tension was recorded till an equilibrium value was reached. At numerous mole fractions of CTAB, the CMC values were measured at piercing disruption ideas in surface tension against the logarithm of concentration.

3.4 Rheological Measurements

All rheological dimensions were achieved by stress controlled TA HR-2 Discovery Hybrid Rheometer. Generally this rheometer has different operating test mode like flow, ramp, and oscillation. In a different mode, we can perform different operations. Rheometer can be equipped with different geometries like cone and plate, parallel plate, concentric cylinder and double gap cylinder. In this measurement cone and plate, geometry was used. Cone plate geometry has 40 mm cone diameter and cone angle (deg:min:sec) 2: 0: 25. Cone and plate geometry are rheologically more correct because the angled cone gives an even shear field. Simultaneously it has drawback also that you can't alter the gap. When liquid is positioned on a horizontal plate and shallow cone placed into it. As the angle fashioned by the surface of the cone and the plate is of the order 1 degree; it is a very shallow cone. Principally when the plate is exchanged, the force on cone measured. Cone dimensions and Rotational speed give the shear rate. This rheological characterization includes the determination of relative viscosity, effect of temperature on viscosity, Oscillatory Rheology. All the experiments were carried out at 25˚C.

CHAPTER 4

CMC of Mixed Surfactant Solutions

4.1 Introduction

The strength of interaction and nature among two surfactants may be decided by the values of interaction parameterβ. Rendering to Rubingh [31], If two surfactants are assorted together, it's mixed CMC (C*) values are given by the equation [2],

$$\frac{1}{C^*} = \frac{\alpha_1}{f_1 C_1} + \frac{(1-\alpha_1)}{f_2 C_2}, \qquad [1]$$

Where $\boldsymbol{\alpha}_1$ is the mole fraction of surfactant 1 in total mixed solute, f1 and f2 are the activity coefficients of surfactants 1 and 2, respectively, and C1 and C2 are the CMC of surfactants. In ideal case f1= f2=1; hence equation (1) becomes,

$$\frac{1}{C^*} = \frac{\alpha_1}{C_1} + \frac{(1-\alpha_1)}{C_2}. \qquad [2]$$

For mixed surfactant system, CMC can also be determined by surface tension concentration curves [3, 13]. On the basis of Rubingh's [31] theory, X_1 is the mole fraction of surfactant 1 in a mixed micelle and easily calculated from the following equation:

$$\frac{{x_1}^2 \ln\left(\frac{\alpha_1 C_{12}}{x_1 C_1}\right)}{(1-x_1)^2 \ln\left(\frac{(1-\alpha_1)C_{12}}{(1-x_2)C_2}\right)} = 1 \qquad [3]$$

So, Substitute the value of X1 into equation (4), it gives the value of interaction

Parameter β for each mole fraction.

$$\beta = \frac{\ln\left[\frac{C^* \alpha_1}{C_1 X_1}\right]}{(1-X_1)^2} \quad \ldots\ldots\ldots \qquad [4]$$

The degree of interaction β between the surfactants is important to their deviation from ideal behaviour. The Positive values show antagonism, and negative values indicate synergism.

4.2 Results and Discussion

4.2.1 CMC values of mixed surfactants

The surface tension values for 3:7 and 7:3 mole ratios of CTAB to IGEPAL CO 890 were experimentally calculated and plotted against the concentration of mixed surfactants in Fig 4.1 to find CMC. Individual surfactant CMC also calculated and plotted.

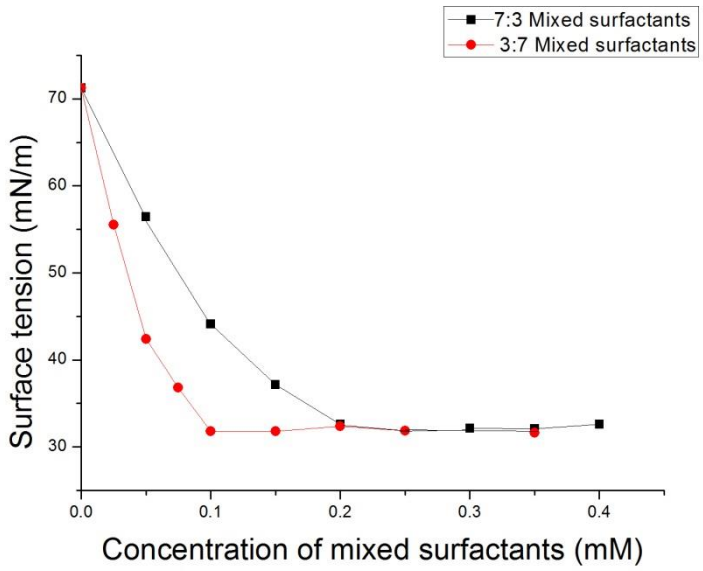


Figure 4.1 Surface tension versus concentartion of various surfactants.

From Fig. 4.1 we can analyse calculated CMC's of 3:7 and 7:3 ratios of CTAB and IGEPAL CO 890 are at 0.1 and 0.2 mmol respectively. Ideal CMC's of surfactants was designed by equation (2). The experimentally attained CMC values for mixed surfactant solutions of CTAB and IGEPAL CO 890 as a function of the mole fraction of CTAB are exposed in the Fig. 4.2. Individual CMC of CTAB and IGEPAL CO-890 are at 0.9 and 0.25 mmol respectively. It is observed that mixed CMC values obtained experimentally are lower than those gained by assuming ideal behaviour [32-34]. The investigational results also show that for 7:3 molar ratios of mixed surfactants the CMC is higher than that of 3:7 molar ratios of mixed surfactants. The record mechanistic reason for the reduction of CMC value is because of the decrease in repulsion between ionic heads due to the insertion of non-ionic heads in amongst them. As non-ionic Surfactants have low CMC than ionic surfactants. The interaction parameter (β) was estimated from Rubingh's equation of regular solution model.

Likewise surface excess (γ_{CMC}) in mol m^{-2} and surface area (*A*min) in nm^2 for pure and mixed surfactant solutions gauged from plot of surface tension *vs* logarithm of surfactant concentration (plot not shown here) are listed in Table 4.1 by using Gibb's surface excess equation.

$$\Gamma = -\frac{1}{n2.203RT}\frac{d\gamma}{d\log C} \quad [5]$$

$$A_{\min} = \frac{1}{N_A \Gamma max} \quad [6]$$

Where R is universal gas constant (8314 m^3 Pa Kmol $^{-1}$ K^{-1}), T is the absolute temperature (K) and NA is the Avogadro number ($6.023*10^{23}$).

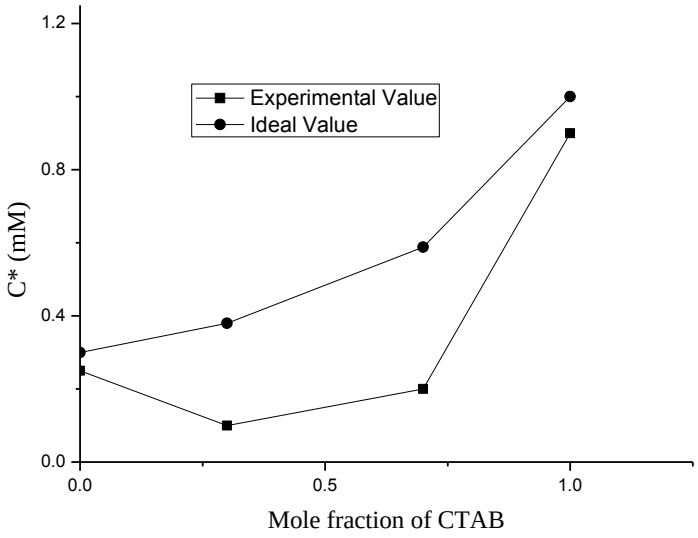


Figure 4.2 Variation of the critical micelle concentration with the mole Fractions of CTAB for the CTAB / IGEPAL CO 890 system.

The value of n is unlike from each surfactant solution, n=1 for non-ionic IGEPAL CO-890 and n=2 for ionic CTAB and mixed surfactants [35]. A_{min} denoted the lowest employed surface area of a molecule at the air-water interface in nm^2. The smallest surface tension values also observed for mixed surfactant solutions as compared to individual surface tension values of surfactant.

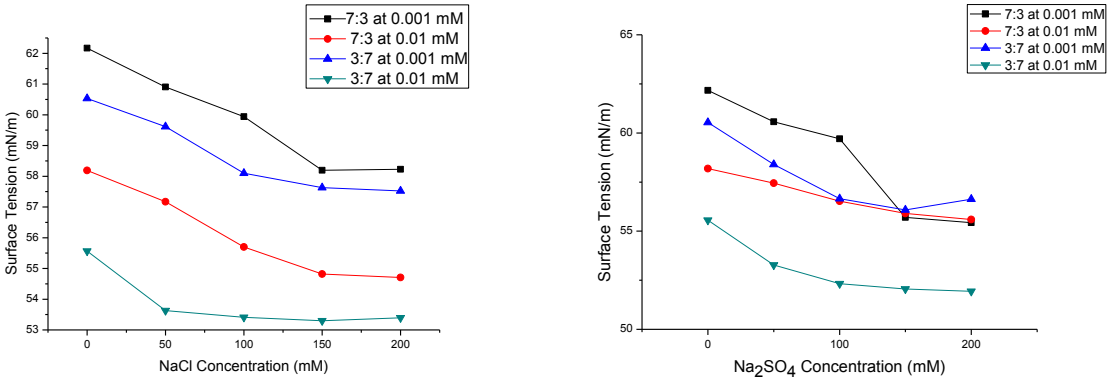
Table 4.1 Values of surface tension, interaction parameter, critical micellar concentration (CMC), surface excess, and area occupied per surfactant molecule for pure and mixed surfactant solutions

Mole fraction (CTAB)	CMC (experimental)	CMC (Theoretical)	Interaction parameter (β)	Surface Tension (y)	Surface Energy $\Gamma_{max} * 10^{-6}$ (mol m^{-2}) of CTAB	Area per molecule (nm^2)
0	0.25	0.3	-	38.11	2.60	0.63
0.3	0.1	0.38	-6.667263	31.815	1.67	0.99
0.7	0.2	0.588	-4.3594180	32.612	1.59	1.04
1	0.9	1	-	32.75	1.70	0.96

It's stimulating to memo that the β values are fewer negative with a change in mole fraction of CTAB. These negative standards of β indicate that there is an attractive interaction (cationic-non-ionic interaction) among the surfactant molecules in the mixed micelle. The repulsion effect develops additional noticeable in a higher mole fraction of CTAB as the addition of cationic head groups in repulsion. The addition of cationic head groups decreases the constancy of mixed micelles and changes the interaction parameter (β) values. The β parameter is more negative (-6.6672) for the 3:7 mixed solution since of its higher synergetic effect. As a result the value of surface excess is maximum and the area engaged by the surfactant molecules at the air–water interface is minimum. Similarly, for 7:3 mixed solution the interaction parameter (β) is less negative (-4.3594), which result in the maximum surface area. Also surface excess decreases with increase in mole fraction of CTAB. These different trends are observed maybe because of less synergetic effect in 7:3 mixed solutions. Also less synergetic effect attributed to the presence of a lesser amount of non-ionic surfactant and increment in the repulsive force among the charged head groups of ionic surfactant molecules.

4.2.2 Effect of electrolytes on the mixed surfactant solutions

(a) (b)



(C)

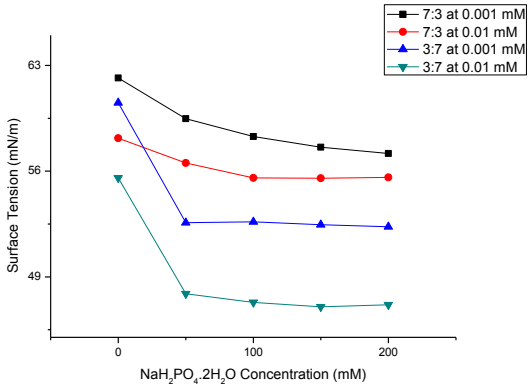


Fig. 4.3 Variation of surface tension at different concentrations of (a) NaCl (b) Na_2SO_4 (c) $NaH_2PO_4 \cdot 2H_2O$ electrolytes when mixed surfactants concentration kept constant a) 0.001 mM b) 0.01 mM

The effect of different electrolytes NaCl, Na_2SO_4 and $NaH_2PO_4 \cdot 2H_2O$, has been studied at two surfactant concentrations 0.001 and 0.01 mmol, and the reduced values of CMC were obtained and plotted in the figure 4.3. The above graphs show that in the attendance of electrolytes, there are additional reductions in surface tension with swelling electrolytes concentration compared to the mixed solutions without the electrolyte [36]. For a static concentration of surfactant mixture with the increasing electrolyte concentration, in the occurrence of a tri-valent counter-ion (PO_4^{3-}), reduction in the surface tension and contact

angle are extra associated to the mono-valent (Cl^-) and di–valent (SO_4^{2-}). It was experiential that the CMC values for a constant surfactant concentration was lowest for $NaH_2PO_4 \cdot 2H_2O$ while for NaCl and Na_2SO_4 the values were found to be almost same. The ultimate surface tension value develops continual at a certain electrolyte concentration for two different concentrations of mixed surfactants tried here, but the plateau values and the essential electrolyte concentration decrease with increasing total mixed surfactant concentration. As an example, for 3:7 and 0.001 mM surfactant concentration in the presence of 200 mM NaCl, the ultimate surface tension is 57.522 mN m^{-1}, whereas in the presence of 200 mM Na_2SO_4 and $NaH_2PO_4 \cdot 2H_2O$ those values reduce to 56.625 mN m^{-1} and 52.327 mN m^{-1} respectively. When the surfactant concentration is ten times higher (0.01 mM), the surface tension decreases to the values of 53.393 mN m^{-1} at 200 mM NaCl, whereas they are 51.933 mN m^{-1} and 47.153 mN m^{-1} at the same concentration of Na_2SO_4 and $NaH_2PO_4 \cdot 2H_2O$ respectively; however, these saturation values are still higher compared to the values of the CMC (0.2 mM) of the same surfactant composition deprived of any electrolyte solution. This can be attributed to the fact that at a very low surfactant concentration, even in the presence of a high electrolyte concentration, the adsorption of surfactant molecules at the interfaces could not reach the saturation level. Hence, from these results it can be concluded that the decrease in value of surface tension in the attendance of electrolytes is mainly because of the reduction in the repulsive force between the surfactant head groups by the counter-ions of the different electrolytes at both the interfaces. The valency of the counter-ion is another important factor that leads to the reduction in the surface tension, as the effective charge density is high for the higher-valency ions, which in turn greatly reduces the obligation of electrolytes to screen the charge of the surfactant head groups. The most mechanistic reason for the reduction of CMC value is because of the discount in repulsion between ionic heads due to the insertion of nonionic heads in between them.

Chapter 5

Oscillatory Rheology

5.1 Introduction

In numerous industrial requests such as cosmetics, pharmaceutical and food, some materials such as emulsions, colloidal suspensions, foams or polymer system are highly significant. Their macroscopic mechanical behaviour is a vital stuff that often determines the usability of such material for given industrial application. It characterized the mechanical behaviour of soft material by the fact that many materials are viscoelastic. All mechanical properties are analysed by applying stress and evaluating its strain. When we use external force to the surface of the bulk material, inside stress arises by different mechanisms. Stress inside a material may occur due to different mechanisms such as external forces applied to the bulk material (like gravity) or friction). Strain rate is the rate of change in strain (deformation) of a material with respect to time. It is possible to recognize the viscous-like and elastic like properties of a material at different time ranges by using oscillatory rheology. It is a much more valuable tool for understanding the dynamics and structural properties of the system. All mechanical properties are analysed by applying stress and evaluating its strain.

5.2 Results and Discussion

The fundamental principle of an oscillatory rheometer is to induce a sinusoidal shear deformation in the sample and measure the resultant stress response. Viscoelastic materials show a response that contain both in-phase and out of phase. The viscoelastic behaviour of the system at ω is characterized by the storage G' (ω), and the loss modulus G" (ω), which respectively characterise the solid-like and fluid like contributions to the measured stress response. The elastic portion represented by storage modulus and viscous part represented by loss modulus. A viscous part also describes the Energy dissipated by heat [11]. The tensile storage and loss moduli are defined as follows:

- Storage: $E'=\sigma_{0/}\varepsilon_0 \cos\delta$
- Loss: $E''=\sigma_{0/}\varepsilon_0 \sin\delta$

Complex Variables can be used to express loss modulus and storage modulus.

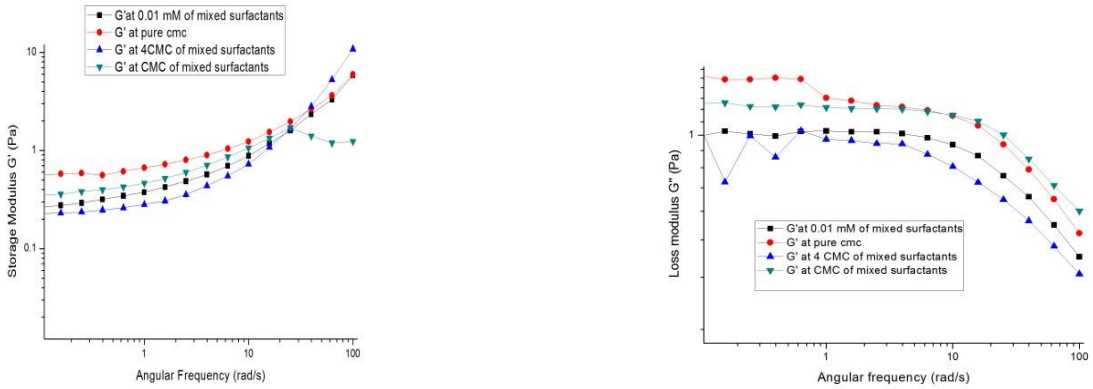
$G*=G'+iG''$

where i is the imaginary unit.

Since 3:7 ratio of mixed CTAB: IGEPAL CO-890 gives optimized CMC value at 0.1mmol concentration, thus the rheological properties of present investigation concerns over the mixed surfactant ratio of 3:7. Due to biodegradable and bio compatible features of IGEPAL and considering economical aspect of cationic surfactant, CTAB, 3:7 ratio of mixed surfactant solutions has been studied with the analysis of rheological properties along with carboxymethyl cellulose for higher end applications such as food, pharmaceutical, cosmetic etc.

5.2.1 Effect of mixed surfactants on rheology of carboxymethyl cellulose (cmc)

5.2.1.1 Constant Amplitude Sweep



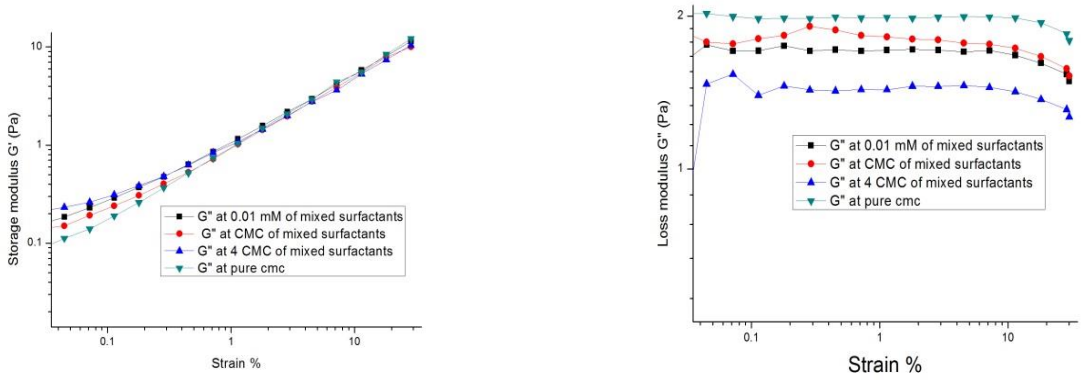
(a) (b)

Fig. 5.1 Effect of mixed surfactant (3:7) solutions on (a) Storage modulus G', (b) Loss modulus G" of cmc at 25˚C

Constant amplitude was set at 2.85 strain % with angular frequency changing from 0.1 to 100 rad/s. All the quantities were done at 25˚C. The storage modulus (G') and loss modulus (G") as a purpose of frequency in the logarithmic plot are reported in Fig. 5.1. The sample was exposed to lower deformation oscillations covering a certain range of frequencies to assess the structural response to deformations of variable timescales. The graphic illustrates the technique to differentiate between the "relaxable" structure found in a cmc solution with mixed surfactant (where cmc disentangle to dissipate stored stresses) and the more permanent elasticity found in a flocculated suspension of pure cmc sample [37]. As we gradually increase the surfactant concentration, storage modulus (G') value of carboxymethyl cellulose gets decreased at initial but gradual enhancement in G' value has been demonstrated at regular increment in angular frequency. As G' is a measure of elastic nature, it is obvious that the

addition of the surfactant is causing the loss in the network structure of cmc polymer [38]. Similarly, loss modulus (G") also provided higher value initially at pure cmc but after certain time interval, with increasing the surfactant concentration, loss modulus mitigates illustrates the viscoelastic properties affecting the recovery of elastic behaviour of cmc due to the addition of various concentration of mixed surfactant solution.

5.2.1.2 Constant Frequency Sweep



(a) (b)

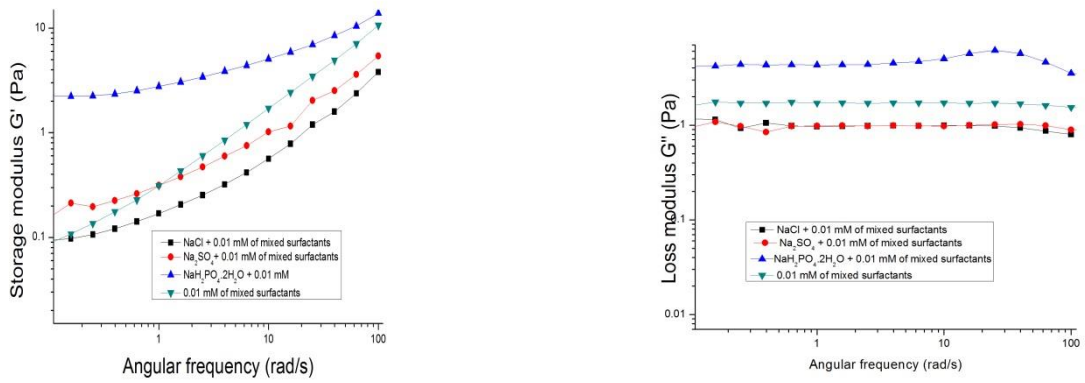
Fig. 5.2 Effect of mixed surfactant (3:7) solutions on (a) Storage modulus G' (b) Loss modulus G" of cmc at 25˚C

Constant frequency was set at 10 rad/s with oscillation strain % varies from 2.8544 to 285.44%. All the measurements were done at 25˚C. The graphical representation has been expressed as logarithmic plot shown in Fig. 5.2. The storage modulus (G') and loss modulus (G") as a function of strain percentage are plotted for pure cmc with the successive addition of the mixed surfactant at various concentrations. Graphic for constant frequency sweep exemplifies the moduli as ability to store and recover deformation energy in an elastic manner. This is directly related to the extent of cross-linking, as the degree of cross-linking gets higher, the storage modulus increases respectively [39]. The addition of the surfactant may enhance the surface viscoelasticity for the adsorbed layer of cmc and the mixed surfactants adsorb at the relatively higher pace to the surface [40]. With contrary to constant amplitude sweep, as we gradually increases the surfactant concentration, storage modulus (G') value of carboxymethyl cellulose increases and similar trends of elastic properties has been illustrated by lowering in the loss modulus (G") values as well. The trend signifies the molecular stretching ability between pristine cmc and mixed surfactant concentrations, to the

extent of shear strain that is recoverable due to the affinity of surfactant molecule to occupy the voids in between cmc molecule, thus enhances the storage modulus trend at various strain percentage.

5.2.2 Effect of electrolytes with mixed surfactant on rheology of Carboxymethyl cellulose (cmc)

5.2.2.1 Constant Amplitude Sweep



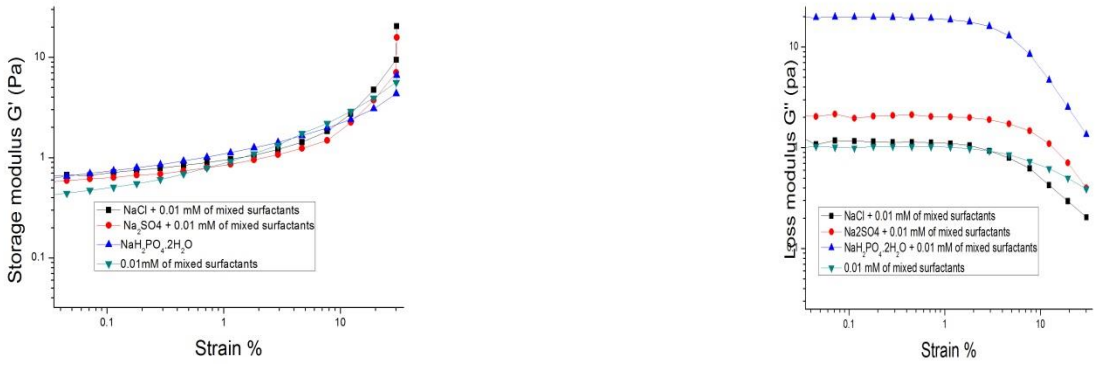
(a) (b)

Fig. 5.3 Effect of electrolyte solutions (3:7 mixed surfactants) on (a) Storage modulus G' (b) Loss modulus G'' of cmc at 25˚C

Constant amplitude was set at 2.85 strain % with angular frequency changing from 0.1 to 100 rad/s. All the measurements were done at 25˚C. The storage modulus (G') and loss modulus (G'') as a function of frequency in the logarithmic plot are reported in Fig. 5.3. 0.01 mMol of mixed surfactant with and without electrolytes illustrates the higher rate of enhancement at trivalent electrolyte mixture. Compared to pure mixed surfactant, an addition of electrolytes enhances the storage modulus due to hydrophobic interaction. With increasing salt concentration, valency increases and cationic CTAB and salt ion interaction elongates the stretching and elastic property. Transportation of the surfactant molecules under the application of shear causes no sliding between the flowing monolayer and the aqueous phase. All the water molecules close to the interface and surrounding molecules of surfactant behave as if they are firmly bound to the molecules of surfactant in the monolayer. When ionic surfactant molecules with electrolyte ions are adsorbed at the interface, the hydrophobic interaction of double layer can extend up to multiple of nanoscale. Thus, a force has been

imparted on the counterions of the double layered cationic surfactant containing electrolyte and induces motion due to the shifting in the monolayer of cation of CTAB. As a result, the flow in the monolayer, for a given shear field, would be higher in the presence of this electrostatic double layer effect [41]. Therefore, the presence of the electrostatic double layer of mixed surfactant comprising highest valence electrolyte makes the interface more elastic in nature.

5.2.2.2 Constant Frequency Sweep



(a) (b)

Fig. 5.4 Effect of electrolyte solutions (3:7 mixed surfactants) on (a) Storage modulus G' (b) Loss modulus G'' of cmc at 25 ˚C

Constant frequency was set at 10 rad/s with oscillation strain % varies from 2.8544 to 285.44%. All the measurements were done at 25˚C. The graphical representation has been expressed as logarithmic plot shown in Fig. 5.4. The storage modulus (G') and loss modulus (G'') as a function of strain percentage are plotted for 0.01 mMol of mixed surfactant and with the successive addition of electrolytes having different valencies. The similar trait of moduli has been observed for constant frequency sweep the same constant amplitude sweep. The plot signifies the enhacement in the solution and rheological properties of mixed surfactant by the addition of electrolyte. The highest trivalent radical of NaH_2PO_4. $2H_2O$ induces hydrophobic interaction and incresases charge density with cationic CTAB surfactant [42]. Thus, increses the storage modulus exemplifies the elasticity of shear thinning liquid of mixed surfactant containing electrolyte with natural additive cmc.

CHAPTER 6

CONCLUSION

Study of mixed surfactants was done in the absence and presence of electrolytes and different properties such as CMC values, interaction parameters, surface excess area and particle area were observed. As the CMC and surface tension values of mixed surfactants were found to be lower than that of the individual values they can be used in a wide range of applications. As cationic surfactants are more economical in comparison to that of non-ionic surfactants a ratio of 7:3 was found to be better than that of 3:7 molar concentration. Oscillatory Rheological studies of carboxymethyl cellulose was also studied in the presence of mixed surfactants and electrolytes and a significant change in storage modulus (G') and loss modulus (G") as well the internal structure due to additives were observed. The study of moduli; storage (G') and loss (G") modulus exemplifies the elastic behaviour of mixed surfactant over natural additive cmc. Further, effect of electrolytes addition with mixed surfactants shows enhancement in storage modulus and loss modulus.

Future interest and progress in understanding of phenomena in mixed surfactant systems seems assured. This projection is based on the importance and increasingly sophisticated use of mixed surfactant systems in practical applications, and growing interest in the experimental and theoretical problems posed by these complex systems. Some of the areas likely to be addressed include surfactant polydispersity, mixtures with unusual surfactant types, adsorption at various solution interfaces including both hydrophilic and hydrophobic solids and liquids, contact angles, and solubilisation phenomena. We believe there will be several major themes in future developments toward understanding mixed surfactant systems.

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